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Laboratoire de Chimie de Coordination
UPR 8241 liée par conventions à l'Université Paul Sabatier
et à l'Institut National Polytechnique de Toulouse

205, route de Narbonne 31077 TOULOUSE CEDEX - FRANCE
Tel : (33) 61 33 31 23 - Fax : (33) 61 55 30 03

Dr. Jean-Pierre MAJORAL
Dr. Anne-Marie CAMINADE

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Phosphorus containing dendrimers: surface chemistry and applications

Abstract

Several methods of grafting phosphonate groups at the surface of a number of dendrimers are reported. Eleven new macromolecules were prepared, possessing either phosphonate groups and hydroxyl groups or phosphonate groups and amino groups. Thus, up to 96 groups of these types were anchored at the surface. All these new compounds were fully characterized by NMR, IR, elemental analysis.

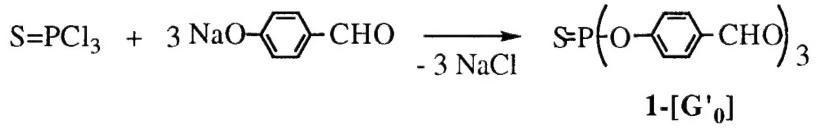
Introduction

The first objective of the work was to graft at the surface of dendrimers various main group element groups and specially phosphorus groups such as phosphonates, phosphates, phosphinates, phosphines.

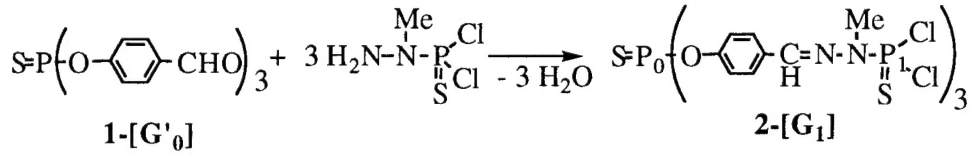
We started our experiment with the anchorage of phosphonate groups because phosphonates are well known for their numerous applications mainly as adhesives (acidobasic type reactions), additives and flame retardants. The high density of surface groups in our dendritic systems should allow the improvement of the properties already shown by the corresponding monomers or to bring new ones.

I - Synthesis of dendrimers

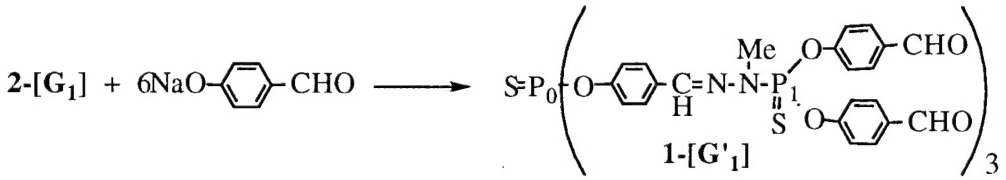
Dendrimers from generation 0 to generation 5 were prepared according to the following reactions (Table I).



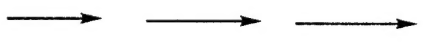
1-[G'$_0$]



1-[G'$_0$] **2-[G$_1$]**



1-[G'$_1$]



1-[G'$_5$]

Generation n =	1	2	3	4	5
(Cl) Number	**2-[G$_1$]**	**2-[G$_2$]**	**2-[G$_3$]**	**2-[G$_4$]**	**2-[G$_5$]**
(CHO)	**1-[G'$_1$]**	**1-[G'$_2$]**	**1-[G'$_3$]**	**1-[G'$_4$]**	**1-[G'$_5$]**
Number of Cl or CHO	6	12	24	48	96
Molecular weight (terminal Cl)	909	2389	5349	11269	23108
Molecular weight (terminal CHO)	1423	3417	7405	15381	31331

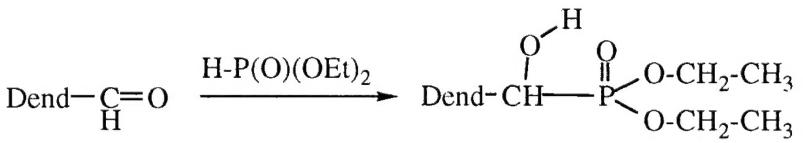
***Table 1**: Some characteristic data concerning dendrimers **2-[G$_1$-G$_5$]** (terminal P-Cl bonds) and **1-[G'$_1$-G'$_5$]** (terminal CHO groups).*

All these dendrimers were characterized by ^{31}P, ^{1}H, ^{13}C NMR, elemental analyses, mass spectrometry (up to [G_2]).

II - Anchorage of phosphonate groups

1 - From terminal aldehyde groups

Several tries were performed to graft in good yields phosphonate groups on the terminal aldehyde groups.



1-[G'$_1$], 1-[G'$_2$]
1-[G'$_3$], 1-[G'$_4$], 1-[G'$_5$]

3-[G'$_1$], 3-[G'$_2$]
3-[G'$_3$], 3-[G'$_4$], 3-[G'$_5$]

This type of reaction was done in several conditions:

* 1 eq. of phosphonate per CHO group, NEt_3 as catalyst, solvent THF, heating 50° then 65° C for 20 h.

* 1.2 eq. of phosphonate per CHO group, DBU as catalyst, solvent THF, 50° then 65° C during 20 h.

* 1.2 eq. of phosphonate per CHO group, CsF as catalyst, 50° then 65° C during 20 h.

All these experiments did not allow us to graft entirely all phosphonate groups. After several attempts, the best method was the following one :

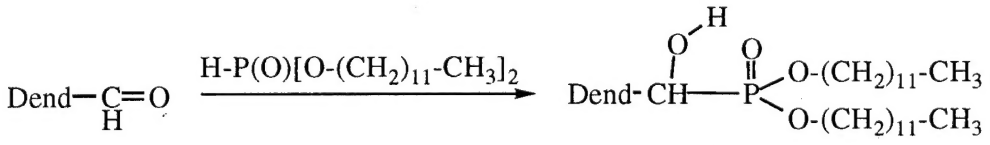
* The dendrimer was dissolved in a mixture of $(EtO)_2P(O)H$, NEt_3, at room temperature, the phosphonate acting as reagent and solvent. This last experiment gave the best results and allowed us to graft from 6 to 96 phosphonates groups (see Table 2).

Generation n =	1	2	3	4	5
Compound	**3-[G_1]**	**3-[G_2]**	**3-[G_3]**	**3-[G_4]**	**3-[G_5]**
Number of terminal phosphonate groups -CH(OH)-P(O)$(OEt)_2$	6	12	24	48	96
Molecular weight	2252	5074	10719	22010	44589

Table 2: *Characteristic data concerning dendrimers with -CH(OH)-P(O)$(OEt)_2$ terminal groups. NMR data are given in the experimental section*

It should be mentioned the interest of this reaction which leads to phosphonate end groups but also to secondary alcohols end groups which should be of help for adhesive properties.

The same type of addition reaction was performed with another phosphonate $(C_{12}H_{25}O)_2P(O)H$ to avoid problems of solubility encountered with $(EtO)_2P(O)H$: compound with 96 CH(OH)-P(O)$(OEt)_2$ groups start to be poorly soluble in common organic solvents and NMR data were collected in CD_3OD.



1-[G'$_1$] **1-[G'$_5$]** → **4-[G'$_1$]** **4-[G'$_5$]**

The grafting of $(C_{12}H_{25}O)_2P(O)$ groups was undertaken on generation **1-[G'$_1$]** and **1-[G'$_5$]** (Table 3) in the same experimental conditions than that used with $(C_2H_5O)_2P(O)H$ and afforded compounds now easily soluble in CH_2Cl_2 or $CHCl_3$.

Generation n =	1	5
Compound number	**4-[G_1]**	**4-[G_5]**
Number of terminal phosphonate groups $CH(OH)\text{-}P(O)(OC_{12}H_{25})_2$	6	96
Molecular weight	3935	71521

***Table 3**: Dendrimers with terminal $CH(OH)\text{-}P(O)(OC_{12}H_{25})_2$ groups*

2 - From terminal imino groups

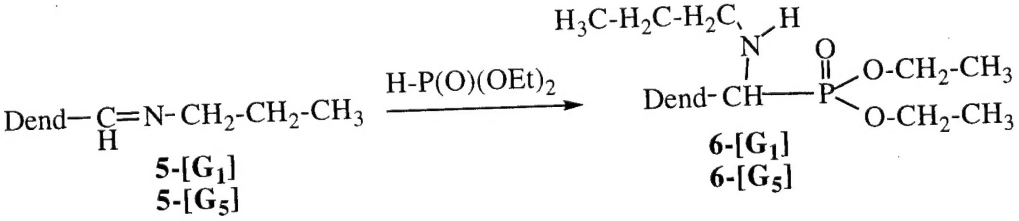
New dendrimers with terminal imino groups were prepared as follows:

$$\text{Dend - CHO} + H_2NC_3H_7 \rightarrow \text{Dend - CH = N-}C_3H_7$$

1-[G'$_1$] **5-[G'$_1$]**

1-[G'$_5$] **5-[G'$_5$]**

Dendrimers **5-[G'$_1$]** and **5-[G'$_5$]** possessing 6 or 96 terminal imino groups respectively were further reacted with $(EtO)_2P(O)H$ again used as solvent. This reaction allowed to obtain new dendrimers **6-[G'$_1$]** and **6-[G'$_5$]** arising from oxidative addition of the P-H bond on imine functions.



Generation n =	1	5
Compound number	**6-[G_1]**	**6-[G_5]**
Number of terminal phosphonate groups -$CH(NHC_3H_7)$-$P(O)(OC_2H_5)_2$	6	96
Molecular weight	2498	48535

***Table 3**: Dendrimers with terminal -$CH(NHC_3H_7)$-$P(O)(OC_2H_5)_2$ groups*

All the new dendrimers, **3-[G_1]**, **3-[G_2]**, **3-[G_3]**, **3-[G_4]**, **3-[G_5]**, **4-[G_1]**, **4-[G_5]**, **5-[G_1]**, **5-[G_5]**, **6-[G_1]**, **6-[G_5]** were fully characterized (see experimental section).

Conclusion

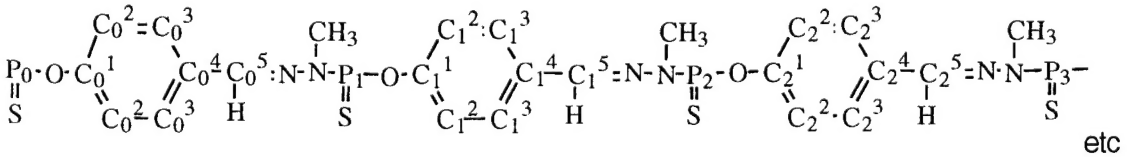
After several attempts, we succeeded in grafting via different ways, phosphonate groups on the surface of our dendritic systems (up to 96 phosphonate groups). Moreover this fruitful method allowed us to graft simultaneously either hydroxyl groups or amino groups which might increase adhesive properties.

Contact will be taken with US Army laboratories for testing the properties of these new macromolecules.

Our next goal for the next three months will consist on the grafting of other phosphorus groups like aminophosphates, phosphates, phosphoniums.

Experimental section

The following numbering scheme is used for NMR



etc

Characteristic NMR data of the main products:

3-[G_1]: ^{31}P {^1H} NMR ($CDCl_3$): δ 21.3 (d, $^7J_{PP}$ = 3.9 Hz, P(O)), 51.8 (s, P_0), 62.0 (t, $^7J_{PP}$ = 3.9 Hz, P_1) ppm. ^1H NMR ($CDCl_3$): δ 1.20 (m, 36H, $C\underline{H}_3$-CH_2-O), 3.30 (d, $^3J_{HP}$ = 10.3 Hz, 9H, P_1-N-CH_3), 3.92 (m, 24H, CH_3-$C\underline{H}_2$-O), 4.90 (s, 6H, O$\underline{H}$), 4.93 (d, $^2J_{HP(O)}$ = 11.5 Hz, 6H, $C_1{}^5$H-P(O)-), 7.15-7.73 (m, 39H, C_6H_4, -$C_0{}^5$H=N-) ppm. ^{13}C {^1H} NMR ($CDCl_3$): δ 16.2 (d, $^3J_{CP(O)}$ = 4.2 Hz, -O-CH_2-$\underline{C}H_3$), 32.7 (d, $^2J_{CP1}$ = 13 Hz, P_1-N-$\underline{C}H_3$), 63.0 (d, $^2J_{CP(O)}$ = 9.6 Hz, O-$\underline{C}H_2$-CH_3), 63.2 (d, $^2J_{CP(O)}$ = 7.9 Hz, O-$\underline{C}H_2$-CH_3), 69.8 (d, $^1J_{CP(O)}$ = 160 Hz, -$\underline{C}_1{}^5$H-P(O)), 121.0 (br s, $C_1{}^2$), 121.3 (br s, $C_0{}^2$), 128.2 (br s, $C_0{}^3$, $C_1{}^3$), 132.5 (s, $C_0{}^4$), 133.8 (br s, $C_1{}^4$), 138.2 (d, $^3J_{CP1}$ = 12 Hz, -$C_0{}^5$H=N-), 150.0 (d, $^2J_{CP}$ = 7.4 Hz, $C_0{}^1$), 150.9 (d, $^2J_{CP}$ = 5.8 Hz, $C_1{}^1$) ppm.

3-[G_2]: ^{31}P {^1H} NMR (CH_2Cl_2): δ 20.8 (d, $^7J_{PP}$ = 3.5 Hz, P(O)), 51.7 (s, P_0), 61.4 (s, P_1), 61.8 (br s, P_2) ppm. ^1H NMR (CD_3OD): δ 1.23 (m, 72H, -O-CH_2-$C\underline{H}_3$), 3.32 (d, $^3J_{HP2}$ = 10.3 Hz, 27H, -P_2-N-$C\underline{H}_3$, P_1-N-$C\underline{H}_3$), 3.98 (m, 48H, -O-$C\underline{H}_2$-CH_3), 5.04 (d, $^2J_{HP(O)}$ = 13.0 Hz, 12H, -$C_2{}^5$H-P(O)), 7.23-7.76 (m, 93H, C_6H_4 and -CH=N) ppm. ^{13}C {^1H} NMR (CD_3OD): δ 17.3 (d, $^3J_{CP}$ = 3.0 Hz, -O-CH_2-$\underline{C}H_3$), 34.1 (d, $^2J_{CP1-2}$ = 12.6 Hz, -P_2-N-CH_3, -P_1-N-CH_3), 64.7 (d, $^2J_{CP(O)}$ = 7.2 Hz, O-$\underline{C}H_2$-CH_3), 65.0 (d, $^2J_{CP(O)}$ = 7.4 Hz, O-$\underline{C}H_2$-CH_3), 71.0 (d, $^1J_{CP(O)}$ = 165 Hz, -$C_2{}^5$H-P(O)), 122.6 (br s, $C_2{}^2$), 123.3 (br s, $C_1{}^2$, $C_0{}^2$), 129.7 (br s, $C_1{}^3$, $C_0{}^3$), 130.2 (d, $^3J_{CP(O)}$ = 3.9 Hz, $C_2{}^3$), 134.0 (br s, $C_0{}^4$, $C_1{}^4$), 136.3 (br s, $C_2{}^4$), 141.2 (d, $^3J_{CP}$ = 11.8 Hz, -$C_1{}^5$H=N-, -$C_0{}^5$H=N-), 151.3 (br s, $C_0{}^1$, $C_1{}^1$), 152.0 (d, $^2J_{CP2}$ = 4.3 Hz, $C_2{}^1$) ppm.

3-[G_3]: ^{31}P {^1H} NMR (CH_2Cl_2): δ 21.2 (d, $^7J_{PP}$ = 3.8 Hz, P(O)), 52.3 (s, P_0), 62.2 (br s, P_1, P_2, P_3) ppm. ^1H NMR (CD_3OD): δ 1.21 (m, 144H, -O-CH_2-$C\underline{H}_3$), 3.22 (m, 63H, P_3-N-CH_3, P_2-N-$C\underline{H}_3$, P_1-N-$C\underline{H}_3$), 4.00 (m, 96H, -O-$C\underline{H}_2$-CH_3), 5.03 (d, $^2J_{HP(O)}$ = 12.6 Hz, 24H, -$C_3{}^5\underline{H}$-P(O)), 7.23-7.67 (m, 201H, C_6H_4 and CH=N) ppm. ^{13}C {^1H} NMR (CD_3OD): δ 17.3 (br s, -O-CH_2-$\underline{C}H_3$), 34.2 (d, $^2J_{CP1-2-3}$ = 10.3 Hz, P_3-NCH_3, P_2-NCH_3, P_1-NCH_3, 64.7 (d, $^2J_{CP(O)}$ = 7.7 Hz, O-$\underline{C}H_2$-CH_3), 65.0 (d, $^2J_{CP(O)}$ = 7.3 Hz, O-$\underline{C}H_2$-CH_3), 71.0 (d, $^1J_{CP(O)}$ = 166 Hz, -$C_3{}^5$H-P(O)), 122.6 (br s, $C_3{}^2$), 123.2 (br s, $C_2{}^2$, $C_1{}^2$, $C_0{}^2$), 130.3 (br s, $C_3{}^3$, $C_2{}^3$, $C_1{}^3$, $C_0{}^3$), 134.1 (br s, $C_2{}^4$, $C_1{}^4$, $C_0{}^4$), 136.3 (br s, $C_3{}^4$), 140.5 (m, -CH=N-), 152.1 (d, $^2J_{CP3}$ = 4.3 Hz, $C_3{}^1$) ppm.

3-[G_4]: ^{31}P {^1H} NMR (CH_2Cl_2): δ 21.2 (d, $^7J_{PP}$ = 4.3 Hz, P(O)), 62.2 (br s, P_1, P_2, P_3, P_4) ppm. ^1H NMR (CD_3OD): δ 1.21 (m, 288H, -O-CH_2-C<u>H</u>$_3$), 3.26 (m, 135H, P_1-N-C<u>H</u>$_3$, P_2-N-C<u>H</u>$_3$, P_3-N-C<u>H</u>$_3$, P_4-N-C<u>H</u>$_3$), 4.00 (m, 192H, -O-C<u>H</u>$_2$-CH_3), 5.03 (d, $^2J_{HP(O)}$ = 12.7 Hz, 48H, -C_4^{5}<u>H</u>-P(O)), 7.25-7.67 (m, 417H, C_6H_4 and -CH=N) ppm. ^{13}C {^1H} NMR (CD_3OD): δ 17.3 (br s, -O-CH_2-<u>C</u>H_3), 34.0 (m, $P_{1\text{-}2\text{-}3\text{-}4}$-N-<u>C</u>$H_3$), 64.7 (d, $^2J_{CP(O)}$ = 7.3 Hz, O-<u>C</u>H_2-CH_3), 65.0 (d, $^2J_{CP(O)}$ = 6.5 Hz, O-<u>C</u>H_2-CH_3), 71.0 (d, $^1J_{CP(O)}$ = 166 Hz, -C_4^{5}H-P(O)), 122.6 (br s, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2), 130.2 (br s, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3), 133.7-134.0 (m, C_0^4, C_1^4, C_2^4, C_3^4), 136.3 (br s, C_4^4), 140.0-141.5 (m, -CH=N-), 152.1 (d, $^2J_{CP4}$ = 5.4 Hz, C_4^1) ppm.

3-[G_5]: ^{31}P {^1H} NMR (CH_2Cl_2): δ 21.3 (d, $^7J_{PP}$ = 4.5 Hz, P(O)), 62.4 (br s, P_1, P_2, P_3, P_4, P_5) ppm. ^1H NMR (CD_3OD): δ 1.20 (m, 576H, -O-CH_2-C<u>H</u>$_3$), 3.25 (m, 279H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$-N-$CH_3$), 4.05 (m, 384H, -O-C<u>H</u>$_2$-CH_3), 5.03 (d, $^2J_{HP(O)}$ = 13.2 Hz, 96H, -C_5^{5}<u>H</u>-P(O)), 7.23-7.67 (m, 849H, C_6H_4 and -CH=N) ppm. ^{13}C {^1H} NMR (CD_3OD): δ 17.3 (br s, -O-CH_2-<u>C</u>H_3), 34.0 (m, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$-$NCH_3$), 64.7 (d, $^2J_{CP(O)}$ = 7.3 Hz, O-<u>C</u>H_2-CH_3), 65.0 (d, $^2J_{CP(O)}$ = 6.5 Hz, O-<u>C</u>H_2-CH_3), 71.0 (d, $^1J_{CP(O)}$ = 166 Hz, -<u>C</u>$_5$^{5}H-P(O)), 122.6 (br s, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2), 130.2 (br s, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3, C_5^3), 133.8-134.1 (m, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4), 136.3 (br s, C_5^4), 140.0-141.0 (m, -CH=N-), 152.1 (br s, C_5^1) ppm.

4-[G_1]: ^{31}P {^1H} NMR ($CDCl_3$): δ 21.2 (d, $^7J_{PP}$ = 3.8 Hz, P(O)), 51.8 (s, P_0), 62.2 (m, P_1) ppm. ^1H NMR ($CDCl_3$): δ 0.85 (t, $^3J_{HH}$ = 5.0 Hz, 36H, -O-$(CH_2)_{11}$-C<u>H</u>$_3$), 1.22 (br s, 216 H, O-CH_2-(C<u>H</u>$_2$)$_9$-CH_2-CH_3), 1.40-1.55 (m, 24H, O-CH_2-$(CH_2)_9$-C<u>H</u>$_2$-CH_3), 3.30 (d, $^3J_{HP}$ = 9.8 Hz, 9H, P_1-N-CH_3), 3.80-3.95 (m, 24H, O-C<u>H</u>$_2$-$(CH_2)_9$-CH_2-CH_3), 4.60 (br s, 6H, -CH-O<u>H</u>), 4.95 (d, $^2J_{HP(O)}$ = 6.5 Hz, 6H, -C_1^{5}H-P(O)), 7.16-7.74 (m, 39H, C_6H_4 and -C_0^{5}H=N-) ppm. ^{13}C {^1H} NMR ($CDCl_3$): δ 13.9 (s, -O-$(CH_2)_{11}$-<u>C</u>H_3), 22.5 (s, O-$(CH_2)_{10}$-<u>C</u>H_2-CH_3), 25.2 (s, -O-$(CH_2)_9$-<u>C</u>H_2-CH_2-CH_3), 28.9 (s, O-$(CH_2)_8$-<u>C</u>$H_2$$(CH_2)_2$-$CH_3$), 29.2 (s, -O-$(CH_2)_7$-<u>C</u>$H_2$-$(CH_2)_3$-$CH_3$), 29.4 (s, -O-$(CH_2)_6$-<u>C</u>$H_2$-$(CH_2)_4$-$CH_3$), 29.5 (br s, -O-$(CH_2)_4$-<u>C</u>$H_2$<u>C</u>$H_2$-$(CH_2)_5$-$CH_3$), 30.3 (s, -O-$(CH_2)_3$-<u>C</u>$H_2$-$(CH_2)_7$-$CH_3$), 30.4 (s, -O-$(CH_2)_2$-<u>C</u>$H_2$-$(CH_2)_8$-$CH_3$), 31.7 (s, -O-$(CH_2)$-<u>C</u>$H_2$-$(CH_2)_9$-$CH_3$), 32.9 (d, $^2J_{CP}$ = 11.6 Hz, P_1-N-<u>C</u>H_3), 66.9 (d, $^2J_{CP(O)}$ = 8.1 Hz, O-<u>C</u>H_2-$(CH_2)_{10}$-CH_3), 67.2 (d, $^2J_{CP(O)}$ = 7.4 Hz, O-<u>C</u>H_2-$(CH_2)_{10}$-CH_3), 70.0 (d, $^1J_{CP}$ = 159 Hz, -C_1^{5}H-P(O)), 121.0 (br s, C_1^2), 121.4 (br s, C_0^2), 128.2 (br s, C_0^3, C_1^3), 132.5 (s, C_0^4), 133.7 (s, C_1^4),

137.9 (br s, $\underline{C}_0{}^5H$=N), 150.0 (br s, $C_0{}^1$), 151.0 (d, $^2J_{CP}$ = 8.6 Hz, $C_1{}^1$) ppm.

4-[G_5]: ^{31}P {^1H} NMR ($CDCl_3$): δ 21.3 (br s, P(O)), 62.6 (m, P_1, P_2, P_3, P_4,P_5) ppm. ^1H NMR ($CDCl_3$): δ 0.84 (br s, 576H, -O-$(CH_2)_{11}$-C$\underline{H}_3$), 1.21 (br s, 3456 H, O-CH_2-(C$\underline{H}_2$)$_9$-CH_2-CH_3), 1.50 (br s, 384H, O-CH_2-$(CH_2)_9$-C$\underline{H}_2$-CH_3), 3.27 (br s, 279H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$-N-C$\underline{H}_3$), 3.90 (br s, 384H, O-C$\underline{H}_2$-$(CH_2)_9$-$CH_2$-$CH_3$), 4.95 (br s, 96H, -$C_5{}^5$H-P(O)), 7.17-7.65 (m, 849H, C_6H_4 and -CH=N-) ppm. ^{13}C {^1H} NMR ($CDCl_3$): δ 13.9 (s, -O-$(CH_2)_{11}$-$\underline{C}H_3$), 22.5 (s, O-$(CH_2)_{10}$-$\underline{C}H_2$-CH_3), 25.2 (s, -O-$(CH_2)_9$-$\underline{C}H_2$-CH_2-CH_3), 28.9 (s, O-$(CH_2)_8$-$\underline{C}H_2(CH_2)_2$-CH_3), 29.2 (s, -O-$(CH_2)_7$-$\underline{C}H_2$-$(CH_2)_3$-CH_3), 29.5 (br s, -O-$(CH_2)_4$-$\underline{C}H_2$-$\underline{C}H_2$-$\underline{C}H_2$-$(CH_2)_4$-CH_3), 30.3 (br s, -O-$(CH_2)_2$-$\underline{C}H_2$-$\underline{C}H_2$-$(CH_2)_7$-CH_3), 31.7 (s, -O-(CH_2)-$\underline{C}H_2$-$(CH_2)_9$-CH_3), 32.5 (m, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$-N-$CH_3$), 66.5 (d, $^2J_{CP(O)}$ = 7.1 Hz, O-$\underline{C}H_2$-$(CH_2)_{10}$-CH_3), 67.1 (d, $^2J_{CP(O)}$ = 6.9 Hz, O-$\underline{C}H_2$-$(CH_2)_{10}$-CH_3), 71.3 (br s, -$C_5{}^5$H-P(O), 121.0 (br s, $C_5{}^2$), 121.7 (br s, $C_0{}^2$, $C_1{}^2$, $C_2{}^2$, $C_3{}^2$, $C_4{}^2$), 128.1 (br s, $C_0{}^3$, $C_1{}^3$, $C_2{}^3$, $C_3{}^3$, $C_4{}^3$, $C_5{}^3$), 132.0 (br s, $C_0{}^4$, $C_1{}^4$, $C_2{}^4$, $C_3{}^4$, $C_4{}^4$), 133.9 (br s, $C_5{}^4$), 137.6-139.4 (m, -CH=N-), 149.9 (d, $^2J_{CP}$ = 7.1 Hz, $C_0{}^1$, $C_1{}^1$, $C_2{}^1$, $C_3{}^1$, $C_4{}^1$), 151.2 (d, $^2J_{CP}$ = 7.2 Hz, $C_5{}^1$) ppm.

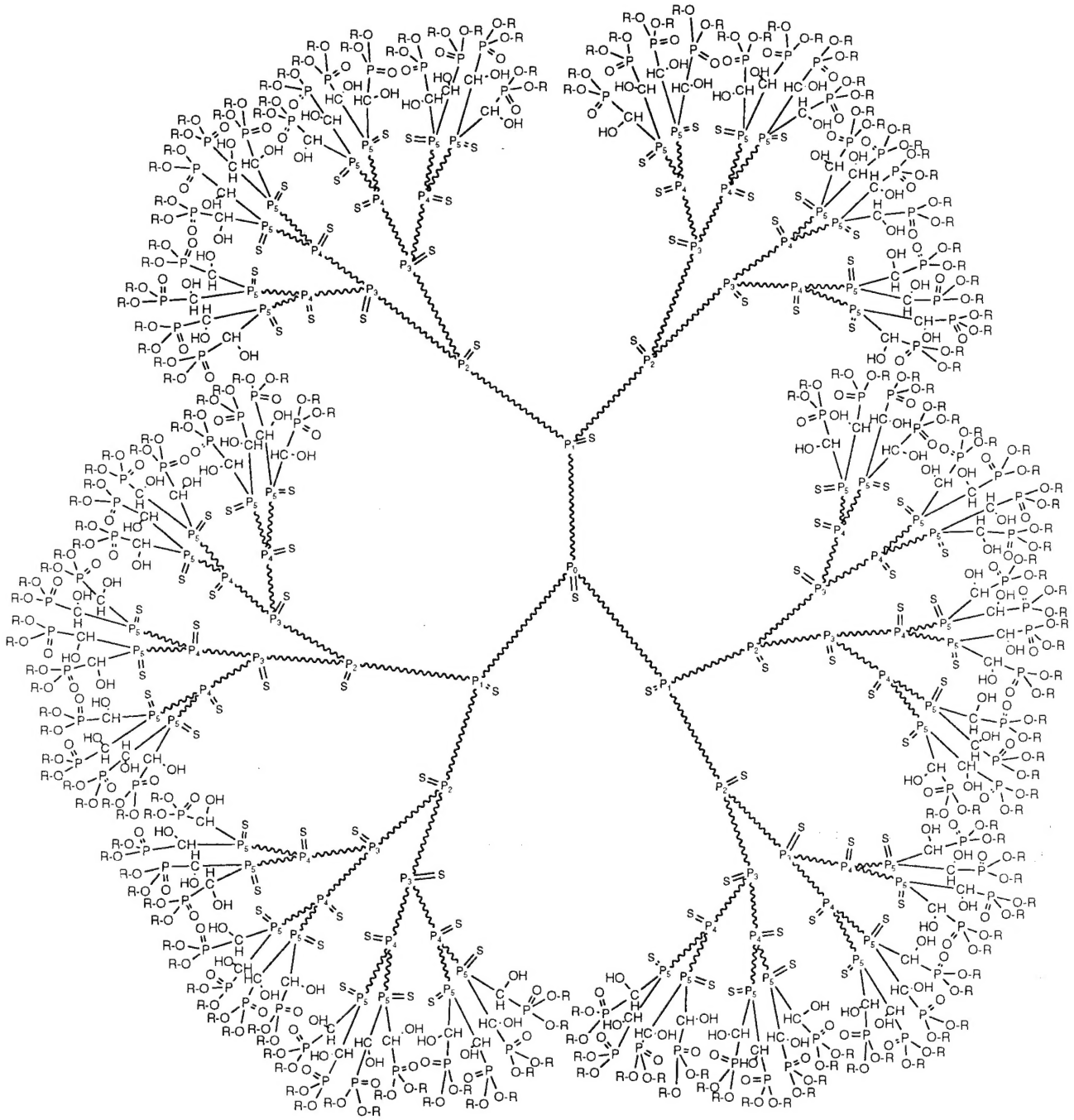
5-[G_1]: ^{31}P {^1H} NMR ($CDCl_3$): δ 52.4 (s, P_0), 61.9 (s, P_1) ppm. ^1H NMR ($CDCl_3$): δ 0.90 (t, $^3J_{HH}$ = 6.7 Hz, 18H, -CH_2-C$\underline{H}_3$), 1.67 (m, 12H, -C$\underline{H}_2$-CH_3), 3.35 (d, $^3J_{HP1}$ = 10 Hz, 9H, -P_1-N-C$\underline{H}_3$), 3.51 (m, 12H, -CH=N-C$\underline{H}_2$-CH_2-CH_3), 7.26-7.70 (m, 39H, C_6H_4 and -$C_0{}^5$H=N-), 8.20 (s, 6H, -$C_1{}^5\underline{H}$=N-CH_2-CH_2-CH_3) ppm. ^{13}C {^1H} NMR ($CDCl_3$): δ 11.7 (s, =N-CH_2-CH_2-$\underline{C}H_3$), 23.8 (s, =N-CH_2-$\underline{C}H_2$-CH_3), 32.9 (d, $^2J_{CP}$ = 13.6 Hz, -P_1-N-CH_3), 63.2 (s, =N-$\underline{C}H_2$-CH_2-CH_3), 121.4 (d, $^3J_{CP}$ = 4.1 Hz, $C_0{}^2$, $C_1{}^2$), 128.3 (s, $C_0{}^3$), 129.2 (s, $C_1{}^3$), 132.4 (s, $C_0{}^4$), 133.5 (s, $C_1{}^4$), 138.4 (d, $^3J_{CP}$ = 14.1 Hz, -$C_0{}^5$H=N-), 151.0 (d, $^2J_{CP}$ = 7.4 Hz, $C_0{}^1$), 152.0 (d, $^2J_{CP}$ = 8.5 Hz, $C_1{}^1$), 159.3 (s, -$\underline{C}_1{}^5$H=N-CH_2-CH_2-CH_3) ppm.

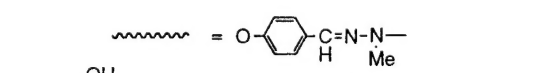
5-[G_5]: ^{31}P {^1H} NMR ($CDCl_3$): δ 61.9 (s, P_5), 62.5 (br s, P_1, P_2, P_3, P_4) ppm. ^1H NMR ($CDCl_3$): δ 0.86 (br s, 288H, N-CH_2-CH_2-C$\underline{H}_3$), 1.61(br s, 192H, -C$\underline{H}_2$-CH_3), 3.28 (br s, 279H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$-N-$CH_3$), 3.47 (br s, 192H, -N-C$\underline{H}_2$-CH_2-CH_3), 7.21-7.65 (m, 849 H, C_6H_4 and CH=N), 8.15 (s, 96H, -$C_5{}^5\underline{H}$=N-CH_2-CH_2-CH_3). ^{13}C {^1H} NMR ($CDCl_3$): δ 11.7 (s, -N-CH_2-CH_2-$\underline{C}H_3$), 23.8 (s, -N-CH_2-$\underline{C}H_2$-CH_3), 32.8 (m, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$-N-$CH_3$), 63.2 (s, =N-C$\underline{H}_2$-$CH_2$-

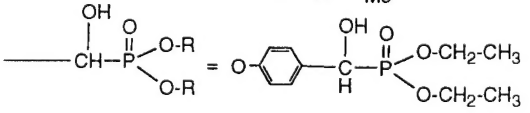
CH_3), 121.4 (d, $^3J_{CP}$ = 4.0 Hz, C_5^2), 121.7 (br s, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2), 128.1 (br s, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3), 129.1 (s, C_5^3), 131.9 (br s, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4), 133.5 (s, C_5^4), 138-139 (m, -CH=N-), 151.2 (d, $^2J_{CP}$ = 4.6 Hz, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1), 151.9 (d, $^2J_{CP}$ = 6.0 Hz, C_5^1), 159.3 (s, -$\underline{C}_5^5$H=N-CH_2-CH_2-CH_3) ppm.

6-[G_1]: ^{31}P {^1H} NMR ($CDCl_3$): δ 23.5 (d, $^7J_{PP}$ = 4.5 Hz, P(O)), 52.6 (s, P_0), 62.5 (m, P_1) ppm. ^1H NMR ($CDCl_3$): δ 0.83 (t, $^3J_{HH}$ = 7.3 Hz, 18H, -CH_2-CH_2-$C\underline{H}_3$), 1.08 (t, $^3J_{HH}$ = 7.0 Hz, 18H, O-CH_2-$C\underline{H}_3$) 1.21 (t, $^3J_{HH}$ = 7.0 Hz, 18H, -O-CH_2-$C\underline{H}_3$), 1.40 (m, 12H, -CH-NH-CH_2-$C\underline{H}_2$-CH_3), 2.11 (s, 6H, NH), 2.41 (m, 12H, -NH-$C\underline{H}_2$-CH_2-CH_3), 3.34 (d, $^3J_{HP}$ = 10.4 Hz, 9H, -P_1-N-CH_3), 3.70-4.08 (m, 30H, -O-$C\underline{H}_2$-CH_3, -$C_1^5\underline{H}$-P(O)), 7.15-7.77 (m, 39H, C_6H_4 and -CH=N-) ppm. ^{13}C {^1H} NMR ($CDCl_3$): δ 11.5 (s, -NH-CH_2-CH_2-$\underline{C}H_3$), 16.1 (d, $^3J_{CP(O)}$ = 6.7 Hz, O-CH_2-$\underline{C}H_3$), 16.2 (d, $^3J_{CP(O)}$ = 6.3 Hz, -O-CH_2-$\underline{C}H_3$), 22.7 (s, -NH-CH_2-$\underline{C}H_2$-CH_3), 32.8 (d, $^2J_{CP}$ = 12.9 Hz, -P_1-N-$\underline{C}H_3$), 49.7 (d, $^3J_{CP(O)}$ = 16 Hz, -NH-$\underline{C}H_2$-CH_2-CH_3), 60.2 (d, $^1J_{CP(O)}$ = 152.7 Hz, -C_1^5P(O)), 62.6 (d, $^2J_{CP(O)}$ = 7.0 Hz, O-$\underline{C}H_2$-CH_3), 62.8 (d, $^2J_{CP(O)}$ = 7.8 Hz, O-$\underline{C}H_2$-CH_3), 121.1 (d, $^3J_{CP}$ = 3.0 Hz, C_1^2), 121.4 (br s, C_0^2), 128.2 (s, C_0^3), 129.4 (d, $^3J_{CP(O)}$ = 5.8 Hz, C_1^3), 132.5 (s, C_0^4), 133.0 (d, $^2J_{CP(O)}$ = 4.3 Hz, C_1^4), 138.2 (d, $^3J_{CP1}$ = 14.5 Hz, -$\underline{C}_0^5$H=N-), 149.9 (d, $^2J_{CP}$ = 6.8 Hz, C_0^1), 150.9 (d, $^2J_{CP}$ = 8.2 Hz, C_1^1) ppm.

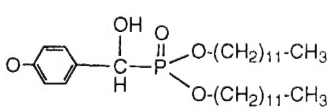
6-[G_5]: ^{31}P {^1H} NMR ($CDCl_3$): δ 22.9 (d, $^7J_{PP}$ = 4.5 Hz, P(O)), 62.1 (br s, P_1, P_2, P_3, P_4, P_5) ppm. ^1H NMR ($CDCl_3$): δ 0.77 (br s, 288H, -CH_2-CH_2-$C\underline{H}_3$), 1.03 (br s, 288H, O-CH_2-$C\underline{H}_3$), 1.18 (br s, 288H, -O-CH_2-$C\underline{H}_3$), 1.45 (br s, 192H, -CH_2-$C\underline{H}_2$-CH_3), 2.3-2.4 (m, 288H, -N$\underline{H}$, -N-$C\underline{H}_2$-CH_2-CH_3), 3.30 (br s, 279H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$-N-$CH_3$), 3.85-4.00 (m, 480H, -O-$C\underline{H}_2$-CH_3, -C_5^5H-P(O)), 7.15-7.65 (m, 849H, C_6H_4 and -CH=N-) ppm. ^{13}C {^1H} NMR ($CDCl_3$): δ 11.4 (s, -NH-CH_2-CH_2-$\underline{C}H_3$), 16.0 (d, $^3J_{CP(O)}$ = 4.7 Hz, O-CH_2-$\underline{C}H_3$), 16.2 (d, $^3J_{CP(O)}$ = 5.1 Hz, O-CH_2-$\underline{C}H_3$), 21.2-22.0 (m, -NH-CH_2-$\underline{C}H_2$-CH_3), 32.6-33.0 (m, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$-N-$CH_3$), 49.3-49.5 (m, NH-$\underline{C}H_2$-$CH_2$-$CH_3$), 59.5 (d, $^1J_{CP(O)}$ = 160 Hz, C_5^5P(O), 62.9 (m, O-$\underline{C}H_2$-CH_3), 121.2-121.6 (m, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2), 128.0 (br s, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3), 129.7 (s, C_5^3), 131.5-131.9 (m, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4, C_5^4), 138.1-139.1 (m, -CH=N-), 150.1-150.3 (m, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1), 151.1 (br s, C_5^1) ppm.







3-[G_5]



4-[G_5]